AD-A277 266

NTATION PAGE

Approved for public release; distribution unlimited

Form Approved
OMB No. 0704-0188

ORT DATE	3. REPORT TYPE AND DATES COVERED
	FINAL 15 Sep 92 TO 14 Sep 93

4. TITLE AND SUBTITLE

Processing boron and boron carbide thin films for protective coatings and device fabrication

5. FUNDING NUMBERS

2305/BS

6. AUTHOR(S)

Professor Peter Dowben

DTIC ELECTE MAR 23 1994 S B D

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Department of Physics & Astronomy
Dept of Physics
Syracuse University
Syracuse, NY 13244-1130

8. PERFORMING ORGANIZATION REPORT NUMBER

AFOSR-TR- 94 0059

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AFOSR/NE
110 Duncan Avenue, Suite B115
Bolling AFB Washington DC 20332-0001

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

F49620-92-J-0503

11. SUPPLEMENTARY NOTES

IOP 339 720

94-09112

12a. DISTRIBUTION / AVAILABILITY STATEMENT

APPROVED FOR PUBLIC RELEASE: DISTRIBUTION IS UNLIMITED

13. ABSTRACT *(Maximum 200 words)*

The fabrication of boron and boron carbide heterojunction devices is based opon the success, thus far, of fabricating boron-carbide heterojunctions in the laboratory of Professor Dowben. We have pioneered the use of heavy boranes, carboranes, and phosphaboranes to make doped layers and semiconductors.

DTIC QUALITY INSPECTED 1

14. SUBJECT TERMS	15. NUMBER OF PAGES
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UNLIMITED

94 3 22 056

YEAR END REPORT. AFOSR Contract # F49-620-92J-0503

"Processing Boron and Boron Carbide Thin Films
for Protective Coatings and Device Fabrication"

P.I. Professor Peter A. Dowben
Department of Physics
Syracuse University
Syracuse, NY 13244-1130
and
Center for Material Research & Analysis
Department of Physics & Astronomy
Behlen Laboratory of Physics
University of Nebraska
Lincoln, NE 68588-0111

The fabrication of boron and boron carbide heterojunction devices is based upon the success, thus far, of fabricating boron-carbide heterojunctions in the laboratory of Professor Dowben. We have pioneered the use of heavy boranes, carboranes, and phosphaboranes to make doped layers and semiconductors [1-3].

A. Introduction and the Current Status of Thin-Film $B_{1-x}C_x$

Boron carbides have remarkable thermal, chemical, and mechanical properties which make them attractive for electronics under extreme conditions. For example, the Vickers hardness ranges from 3.6 x 10^3 to 2.8 x 103 [4] and SiC at 3.5 x 103 [5]. Many techniques have been assessed for depositing boron carbides, including powder metallurgy and a variety of chemical vapor deposition approaches [6-7]. This work has yielded a rather conductive, icosahedral material ($\sigma \sim 1\Omega^{-1}cm^1$ near room temperature) [8-10] with bandgaps varying between 1.9 and 0.6 eV as carbon incorporation increases to about 20%. This material is unsuitable for fabrication of conventional electronic devices (diodes, transistors, etc.), although it does have very favorable properties for thermoelectric converters.

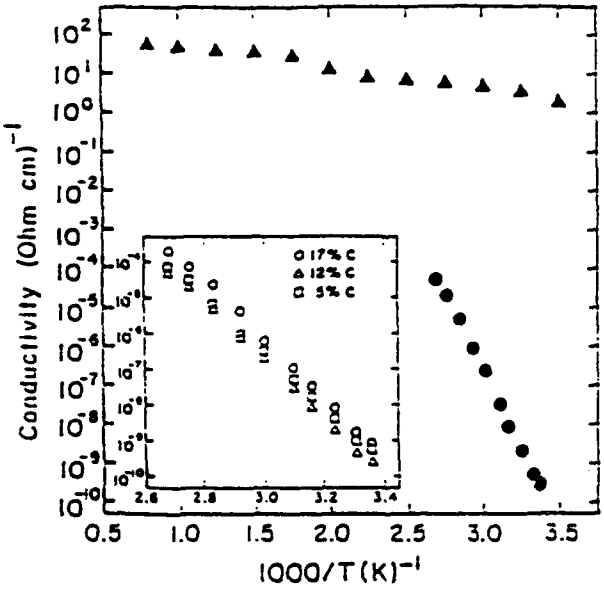

Figure 1: Conductivities versus reciprocal temperature of boron carbide samples (approximately 20 percent carbon) using two different deposition techniques. ( ): Wood and Emin [6]. (Δ): Syracuse work [9]. The conductivities for the plasma enhanced chemical vapor deposited films of different compositions of boron carbides are shown at the insert demonstrating that the conductivities are largely independent of carbon concentration.

With recent AFOSR and NSF funding we have discovered that boron carbide films plasma deposited using pentaborane/methane mixtures yield a boron carbide with qualitatively different electrical properties: this material has a conductivity as low as 10^{-10} $(Ohm\ cm)^{-1}$ [11-13] near room temperature (as seen in Figure 1). We have developed the thin film materials fabrication technology to the point where we have successfully made the first heterojunction diodes employing boron carbide [11-14]. Both the optical and X-ray diffraction studies performed on this new high resistivity form of born carbide indicate that the structure is comparable to that obtained in previous work, and we thus anticipate that favorable mechanical and refractory properties of icosohedral boron carbide will be obtained in the high resistivity form.

Since the 1950s, there has been an effort to exploit boron and boron carbide as a high temperature electronic material (in particular, by the Airforce) [4, 15, 5, 16, 39]. We succeeded [11], based upon the realization that electrical conductivities in boron and boron carbide fabricated by a wide variety of techniques resulted in a material that was probably not compositionally homogeneous. The electrical conductivities in most boron carbides are very high (> 1 Ohm-cm at room temperature) and the mobility is low (< 1 $cm^2/V\text{-}sec$). These undesirable properties of a semiconductor electronic material have been postulated to be the result of inhomogeneity within boron carbide, in particular non-bonding free carbon [17] which resulted in increased electrical conductivity.

Moderate sized borane and carborane cluster molecules, however, looked like feasible source molecules for boron-containing materials [1-3]. These compounds have structures close to the icoshedral structure of the bulk boron and boron carbide materials [21]. The deposition chemistry (i.e. the energetics) and structure of these molecules favors growth of an isotropic boron carbide [19, 20]. We believed that a boron carbide could be fabricated without free carbon or graphitic precipitates because of the experimentally determined chemical thermodynamics of these molecules.

Indeed, the material made by plasma-enhanced chemical vapor deposition of boron carbide from boranes and alkanes was isotropic and uniform [2, 11, 21], even if it was microcrystalline and not crystalline [11, 21]. In spite of the unprepossessing microstructure of the boron carbide and boron thin films formed by CVD from boranes, this material had a resistivity 10 orders of magnitude greater than any boron carbide fabricated up to that point [11] and a band gap that could be altered from 0.8 to 1.9 eV by changing the boron to carbon stoichiometry [2, 11].

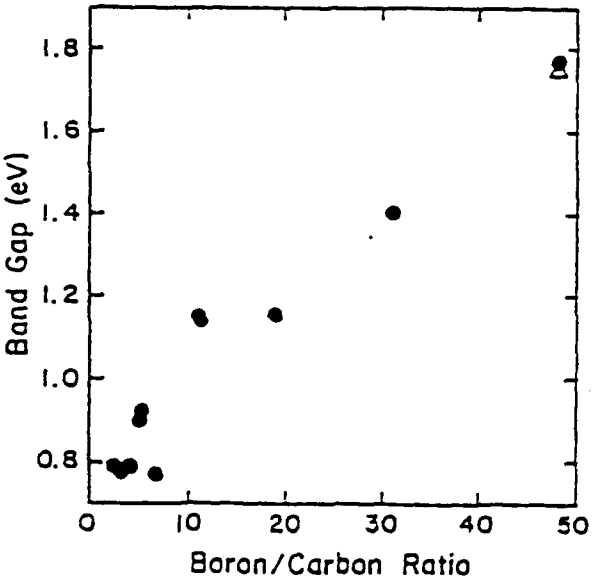

Figure 2: Band gap versus composition

At long last, boron carbide devices could be made, and even though the lattice match is poor, and epitaxial growth is unlikely, boron-carbide on Si(111) (n-typed doped) results in a heterojunction diode [11-13]. This, then became the major focus of the AFOSR-funded research program.

The band gap of boron carbide in our material is close to values predicted theoretically and, consistent with theory, the gap is indirect [35]. Temperature-dependent

conductivity studies indicate that the activation barrier of boron carbide is 1.24 eV, virtually independent of composition [11], but with boron carbide/Si(111) diodes the conductance has an activation barrier half the boron carbide bandgap [12, 13].

B. Fabrication of Devices

The temperature insensitivity of boron carbide devices compares well with diamond heteroepitaxy devices as seen in Figure 3, though clearly heteroepitaxy diamond diodes work at far higher temperatures than boron carbide diode fabricated to date. Heteroepitaxy diamond devices are very expensive by comparison with boron carbide devices because of the cost associated with the preparation of the substrate. As yet, plasma-enhanced chemical vapor deposition (PECVD) diamond devices do not work as well as boron carbide devices in any fabrication approach where significant numbers of defects exist because defects tend to reduce the effective band gap of diamond. Cost factors clearly indicate boron carbide is commercially useful. The temperature range over which boron carbide devices may work could possibly be expanded by using a better thermally matched material such as SiC and the use of this substrate is one of our device fabrication objectives.

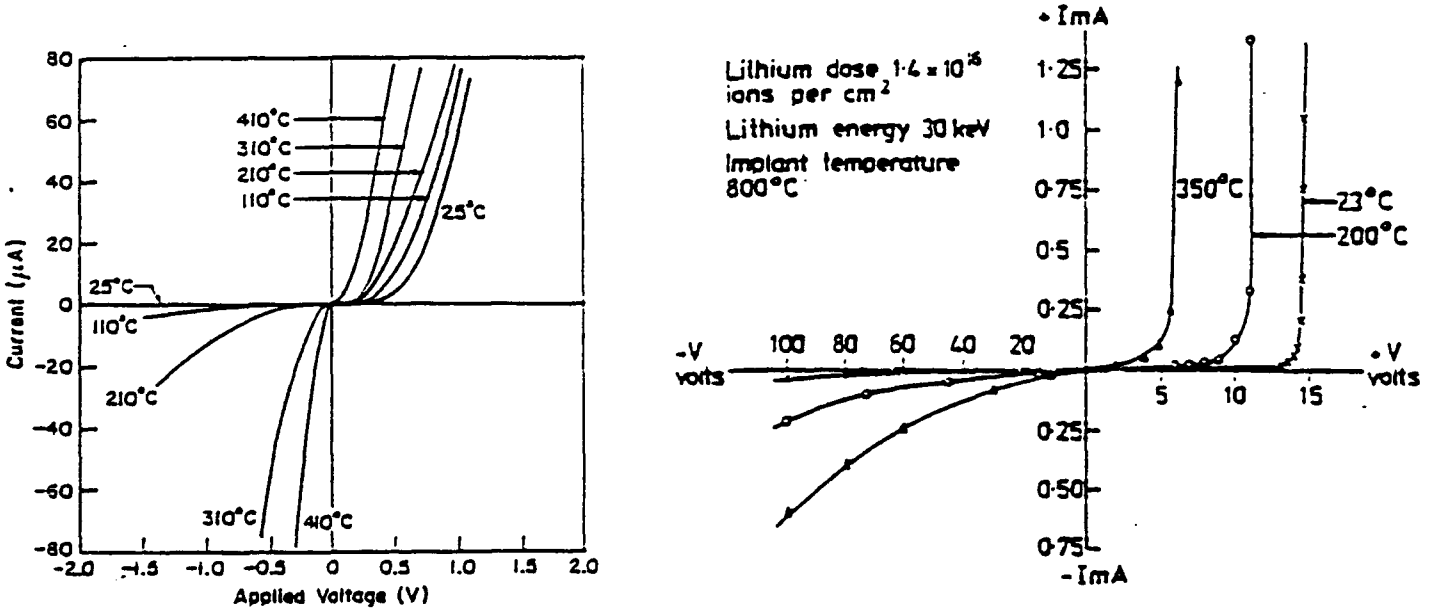

Figure 3: Temperature dependence of $B_{19}C$/Si(111) heterojunction IV-characteristics on the left and heteroepitaxy diamond device are on the right, for comparison.

With wide band gap boron carbide (1.2 eV) the boron carbide/Si(111) heterojunction is temperature insensitive to temperatures above 200°C [12, 13] while smaller band gap boron carbides result in more temperature-sensitive diodes [13].

Boron carbide heterojunction diodes exhibit light-induced effects consistent with changes in the interface depletion layer (as seen in Figure 4). Because of these results, it is clear we can succeed in making a thin film transistor from boron carbide.

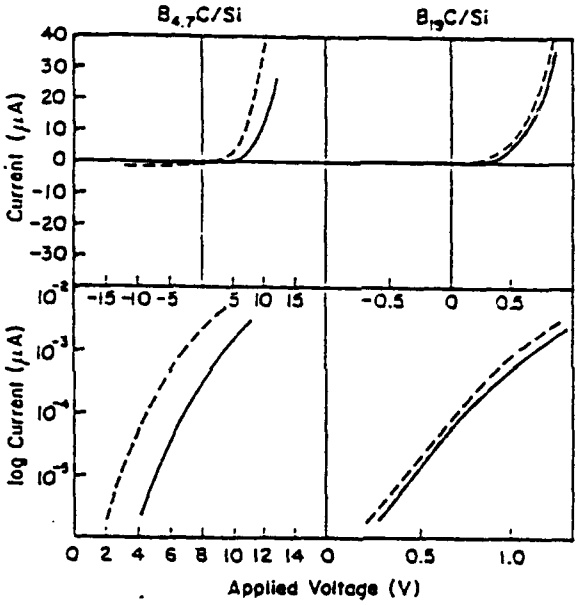

Figure 4: Light dependence of $B_{19}C$/Si(111) diodes. I-V curves were obtained for visible light (- - - -) and dark (————) indicating light sensitivity. Forward bias currents are plotted at the top log scale.

C. Accomplishments

As is clear from the discussion outlined above, we have succeeded under the current AFOSR funding in fabrication of working diodes from a novel semiconductor material. These heterojunction diodes are temperature-insensitive to temperatures well above 250°C. The funding from AFOSR has, in part, contributed to the preparation of four manuscripts submitted for publication. These papers are:

Published

S. Lee, T. Ton, D. Zych, and P. A. Dowben, "Conductance in Microcrystalline $B_{1-x}C_x$/Si Heterojunction Diodes," MRS Symp. Proc. 283, 483, 1993.

In Press

S. Lee, J. Mazurowski, W.L. O'Brien, Q.Y. Dong, J.J. Jia, T.A. Callcott, Yexin Tan, K.E. Miyano, D.L. Ederer, D.R. Mueller, and P.A. Dowben, "The Structural Homogeneity of Boron Carbide Thin Films Fabricated Using Plasma-Enhanced Chemical Vapor Deposition from B_5H_9+CH_4," J. Appl. Phys., in press.

N.M. Boag, and P.A. Dowben, "Designing of Organometallics for Vapor Phase Metallization of Plastics", Metallized Plastics IV. Fundamental and Applied Aspects, edited by K. Mittal, Plenum Press.

Submitted

S. Lee and P.A. Dowben, "The Properties of Boron Carbide/Silicon Heterojunction Diodes Fabricated by Plasma-Enhanced Chemical Vapor Deposition," Appl. Phys. A., submitted.

S. Lee, S.-d. Hwang, P.A. Dowben, Young-Feng Hu, and G.M. Bancroft, "The Electronic Structure of Nido-2,3-dicarbahexaboranes in Different Chemical States," Chem.Phys., submitted.

In addition, the current AFOSR contract has substantially contributed to the education of two students. John Mazurowski received his M.Sc. in Physics on the basis of a thesis funded by AFOSR and a Society for Hybrid Microelectronics Fellowship. He was awarded the Syracuse University Master's Prize for this thesis. Sunwoo Lee obtained his Ph.D. in Solid State Science and Technology, and has been nominated for a Syracuse University Ph.D. prize. Sunwoo Lee has already obtained the New York State American Vacuum Society Prize for outstanding graduate work for his work related to the current AFOSR contract.

D. Summary

We have accomplished a substantial fraction of the goals set out under the current AFOSR contract F49-620-92J-0503. We will accomplish more by the end of the current funding period. Two goals stand out as important to the development of boron carbide as a

semiconductor material. (1) We intend to make a thin film transistor and (2) we need to characterize the transport properties of this novel form of boron carbide.

In the follow-up work, two principal investigators, Professors P.A. Dowben and E.A. Schiff will be dedicated toward these goals. By combining experience of materials fabrication and $B_{1-x}C_x$ heterojunction diode fabrication (with P.A. Dowben) with experience in transport measurements (E.A. Schiff) these goals will be realized.

E. References

[1] Yoon-Gi Kim, P.A. Dowben, and J.T. Spencer, J. Vac. Sci. Technology, A7, 2796

[2] J. Mazurowski, S. Lee, G. Ramseyer, and P.A. Dowben, Mat. Res. Soc. Symp. Proc. 242, 637 (1992); J. Mazurowski, S. Baral-Tosh, G. Ramseyer, J.T. Spencer, Yoon-Gi Kim, and P.A. Dowben, Mat. Res. Soc. Symp. Proc. 190, 101 (1991).

[3] J.T. Spencer, P.A. Dowben, and Yoon-Gi Kim, U.S. Patent 4957 773, September 18, 1990.

[4] F.S. Galasso, *Chemical Vapor Deposited Materials* (CRC Press, New York, 1992).

[5] I.M. Buckley-Golder, et al., *Diamond and Related Mat., 1*, 43 (1991).

[6] Boron Rich Solids, *AIP Conference Proceedings no. 140*, edited by D. Emin, T. Aselage, C.L. Beckel, I.A. Howard and C. Wood, (1986) and the references therein.

[7] Boron Rich Solids, *AIP Conference Proceedings no. 231*, edited by D. Emin, T. Aselage, A.C. Switendick, B. Morosin, and C.L. Beckel, (1991) and the references therein.

[8] C. Wood and D. Emin, Phys. Rev. B29, 4582 (1984); D. Emin, Mat. Res. Soc. Symp. Proc. 97, 3 (1987); D. Emin, in *Boron Rich Solids, AIP Conference Proceedings 231*, 65 (1991); ibid p. 65 (1991); G.A. Samara, H.L. Tardy, E.L. Bendurini, T.L. Aselage, and D. Emin, in: Boron Rich Solids, AIP Conference Proceedings 231, 77 (1991); D. Emin, in: Boron Rich Solids, *AIP Conference Proceedings 231*, 104 (1991).

[9] H. Werheit and K. de Groot, Phys. Status Solidi, B97, 229 (1980); H. Werheit, U. Kuhlmann, R. Franz, W. Winkelbauer, B. Herstell, D. Fister, and H. Neisius, in *Boron Rich Solids, AIP Conference Proceedings 231*, 104 (1991).

[10] L. Zuppiroli, N. Papandreou and R. Kormann, J. Appl. Phys. 70, 246 (1991); A.K. Bandyopadhyay, F. Beuneu, L. Zuppiroli, and M. Beauvy, J. Phys. Chem. Solids 45, 207 (1984); L. Zuppiroli and L. Forro, Phys. Lett. A 141, 181 (1989).

[11] S. Lee, J. Mazurowski, G. Ramseyer, and P.A. Dowben, J. Appl. Phys. 72, 4925 (1992).

[12] S. Lee and P.A. Dowben, Appl. Phys. A, submitted.

[13] S. Lee, T. Ton, D. Zych and P.A. Dowben, Mat. Res. Soc. Symp. Proc. (1993) in press.

[14] H.E. Robson, Ph.D. Dissertation, Univ. of Kansas (1959).

[15] M. Yoder, *Mat. Res. Soc. Symp.* Proc. 97, 210 (1987)

[16] R.J. Starks, J.T. Buford, and P.E. Grayson, "Boron Since Asbury Park: The First International Boron Conference Sept. 18, 1959" in AIP Conference Proceedings vol. 140, Boron Rich Solids, p. 373 (186).

[17] A.K. Bandyopadhyay, F. Beuneau, L. Zuppiroli, and M. Beauvy, J. Phys. Chem. Solids 45, 207 (1884).

[18] A.P. Hitchcock, A.T. Wen, Sunwoo Lee, J.A. Glass, J.T. Spencer, and P.A. Dowben, J. Phys. Chem., submitted; S. Lee, P.A. Dowben, A.T. Wen, A.P. Hitchcock, J.A. Glass, and J.T. Spencer, J. Vac. Sci. Technol. A10, 756 (1992); W. J. Dulmage and W.N. Lipscomb, J. Am. Chem. Soc. 73, 3539 (1951); W.J. Dulmage and W.N. Lipscomb, Acta Cryst. 5, 260 (1952); W.E. Streib, F.P. Boer, and W.N. Lipscomb, J. Am. Chem. Soc. 85, 2331 (1963); F.P. Boer, W.E. Streib, and W.N. Lipscomb, Inorg. Chem. 3, 1666 (1964); J.S. Kasper, C.M. Lucht, and D. Harker, Acta Cryst. 3, 436 (1950); R.K. Hohn and M.D. Bohn, Inorg. Chem. 10, 350 (1971); L.V. Vilkov et al., Zh. Strukt Khim., 7, 5 (1969); V.S. Mastryokov et al., Zh. Strukt. Khim, 10, 136 (1969).

[19] N.N. Greenwood, R. Greatrex, Pure and Appl. Chem. 59, 857 (1987).

[20] Sunwoo Lee, J. Mazurowski, W.L. O'Brien, Q.Y. Dong, J. Jia, T.A. Callcott, Y. Tan, K.E. Miyano, D.L. Edever, D.R. Mueller, and P.A. Dowben, J. Appl. Phys., submitted.

Approved for public release;
distribution unlimited.